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Chemical improvement of surfaces. Part 1: Novel functional modification of wood with covalently bound organoboron compounds*

Jan C. Namyslo and Dieter E. Kaufmann**

Clausthal University of Technology, Institute of Organic Chemistry, Clausthal-Zellerfeld, Germany

**Corresponding author.
Clausthal University of Technology, Institute of Organic Chemistry, Leibnizstrasse 6, D-38678 Clausthal-Zellerfeld, Germany
E-mail: dieter.kaufmann@tu-clausthal.de

Abstract

A novel type of chemical modification of wood was developed and applied to functionalise wood permanently with organoboron compounds. The covalent attachment of metalloid substituents via a benzotriazolyl-activated benzoic acid to wood hydroxy groups was in focus. Thus, standard modification procedures in wood chemistry – such as the acetylation – are improved by avoiding either the loss of half the reagent in the case of acid anhydrides or the release of corrosive hydrochloric acid in the case of carboxylic acid chlorides. The introduced boron moiety could be a contribution to solve a long-lasting problem in the field of wood protection: chemical fixation of an organoboron compound by means of a well-defined covalent bond. Accordingly, the hitherto insufficient long-term availability of conventionally spread boron compounds as wood protecting agents caused by leaching can now be avoided. The investigation was also extended to arylsilyl compounds, as a second type of organometal substances, which potentially allow for subsequent chemical modifications by *ipso*-substitution. The presented wood modification reactions yielded weight percent gain values from 14% to 31% on beech wood, spruce wood, and pine sapwood meal (approximately 500 μm in diameter) or pine sapwood veneer chips. The modified meals and chips were analysed by IR spectroscopy.

Keywords: boron; covalent fixation; leachability; synthesis; wood preservatives.

Introduction

Natural wood is durable only when it is shielded from air, UV light, or other environmental influences including biological attack. However, natural deterioration is difficult to avoid under outdoor conditions and this problem is often tackled by certain types of chemical modification (Rowell 1983, 2006; Hill 2006).

The improvement of flame retardant properties and resistance against voracious beetles, worms, or insects are also a matter of wood protection. The treatment of wood with boron-containing inorganic (Cockcroft and Levy 1973; Pizzi and Baecker 1996; Toussaint-Dauvergne et al. 2000) or organic chemicals (Howell 1988; Lloyd and Deane-Wray 1995; Yalinkilic et al. 1998a) belong to the remedies. Boric acid or organoboronic acid are prominent members of boron-containing wood preservatives, which exhibit exceedingly low toxicity against humans (Thevenon et al. 1998). They have further advantages, such as being odourless, colourless, and non-corrosive (Hashim et al. 1994).

The above-mentioned approaches to wood protection by boron-containing chemicals suffer from subsequent leaching of biologically active agent, even though fixation of boric acid by esterification to some extent has been published in the literature (Pizzi and Baecker 1996; Thevenon et al. 1998; Yalinkilic et al. 1998b). Mixed ammonium salts comprising two types of anions, namely borate and oleate (Lyon et al. 2007), have also been applied.

In the present paper, an alternative protection procedure will be presented, which makes leachability negligible due to a strong covalent bond between a boron-containing biocide and wood. Although the attached chemical linker contains a carboxylic ester unit (established from wood hydroxy groups and an organic acid derivative), the typical disadvantages of common esterification procedures are evaded. In particular, half the reagent is not lost, which is the case by esterification with conventional acid anhydrides and corrosive volatiles (such as HCl) are not produced, which is the case in classical procedures with organic acid chlorides.

Materials and methods

Organic precursors

General procedures Melting points were measured on a Büchi 520 (Büchi, Flavil, Switzerland) apparatus and were uncorrected. NMR spectra: Avance 400 (Bruker, Ettlingen, Germany) with 400 MHz proton frequency. ^{1}H-NMR spectra in $CDCl_3$ were referenced to tetramethylsilane (TMS 0.0 ppm). ^{13}C-NMR spectra refer to the solvent signal centre at 77.0 ppm ($CDCl_3$). In the case of DMSO-d_6, the solvent peak was set to 2.50 ppm (^{1}H) and 39.50 ppm (^{13}C), respectively. For deuterobenzene, these solvent signals were set to 7.16 ppm (^{1}H) and 128.7 ppm (^{13}C), respectively. All coupling constants are given in Hz. IR spectra: 'Vector 22' FTIR (Bruker, Bremen, Germany) as film between NaCl plates or as KBr pellet. Mass spectra: 'HP MS 5989B' (Hewlett Packard, Böblingen, Germany) with direct inlet and

*Dedicated to Professor Ihsan Erden on the occasion of his 60th birthday.

electron impact ionisation (EI). Elemental analyses: Institute of Pharmaceutical Chemistry, Braunschweig Technical University, Germany. Thin layer chromatography (TLC) analyses: TLC plates coated with silica gel (60 F 254) purchased from Merck, Darmstadt, Germany. Silica gel 60 was used for column chromatography (Macherey-Nagel, Düren, Germany). All solvents were dried according to standard methods and were freshly distilled prior to use. Chemicals and solvents were used as purchased from Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany. Wood samples were obtained from the Section of Wood Biology and Wood Products, Georg-August-University Göttingen, Göttingen, Germany.

4-Carboxyphenylboronic acid (2) A solution of 3.40 g (25 mmol) 4-methylphenylboronic acid (**1**) in 75 ml of 3.5% aqueous NaOH was added in one portion to a mixture of 11.85 g (75 mmol) $KMnO_4$ and 250 mg tetrabutylammonium bromide in 250 ml water. Subsequently, the mixture was stirred vigorously for 5 h at 60°C. After cooling down to room temperature (r.t.), 50 ml of ethanol was added. The dark residue, mainly manganese dioxide, was filtered off and disposed. The clear filtrate itself was neutralised with 20% HCl and evaporated to dryness. The resulting crude product was then extracted with diethyl ether (5×200 ml). Thereafter, the combined organic layers were washed with $NaHCO_3$ and dried (Na_2SO_4). Subsequent to evaporation of the solvents, the residue was recrystallised from water and finally dried to yield 3.51 g (85%) of pure **1**. IR (KBr): 3171, 1691, 1563, 1512, 1425, 1401, 1359, 1269, 1191, 1125, 847, 707, 622 cm^{-1}. ^{1}H-NMR (DMSO-d_6, 400 MHz): δ = 7.89 (m, 4H, $H_{arom.}$), 8.27 [s, 2H, $B(OH)_2$], 12.94 (br s, 1H, COOH). ^{13}C-NMR (DMSO-d_6, 100 MHz): δ = 128.1 (2 C, C-3,5), 132.0 ($C_{quat.}$, *C*-CO_2H), 134.2 (2 C, C-2,6), 139.4 ($C_{quat.}$, C-B), 167.5 ($C_{quat.}$, CO_2H). ^{11}B-NMR (DMSO-d_6, 128 MHz): δ = 29.1.

2-(4-Carboxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (3) A mixture of 2.49 g (15.0 mmol) 4-carboxyphenylboronic acid (**2**) and 1.56 g (15.0 mmol) 2,2-dimethyl-1,3-propanediol in 75 ml of anhydrous tetrahydrofuran (THF) were stirred for 15 min at r.t. Subsequent evaporation of the solvent yielded 3.51 g (100%) of pure product **3**. Mp. 236°C. IR (KBr): 2963, 1693, 1506, 1481, 1428, 1305, 1290, 1253, 1132, 933, 859, 718, 705, 641 cm^{-1}. ^{1}H-NMR (DMSO-d_6, 400 MHz): δ = 0.96 (s, 6H, CH_3), 3.77 (s, 4H, CH_2), 7.80 (d, 2H, *J* = 7.8 Hz, $H_{arom.}$), 7.91 (d, 2H, *J* = 7.8 Hz, $H_{arom.}$), 13.00 (br s, 1 H, COOH). ^{13}C-NMR (DMSO-d_6, 100 MHz): δ = 21.3 (2 C, CH_3), 31.5 [$C_{quat.}$, *C*(CH_3)$_2$], 74.5 (2 C, CH_2), 128.4 (2 C, C-3,5), 132.6 ($C_{quat.}$, *C*-CO_2H), 133.6 (2 C, C-2,6), 137.1 ($C_{quat.}$, C-B), 167.4 (CO_2H). ^{11}B-NMR (DMSO-d_6, 128 MHz): δ = 26.8.

4-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)benzoic anhydride (4) In an ice bath, a solution of 6 ml triethylamine in 6 ml of anhydrous THF was added to a mixture of 2.34 g (10.0 mmol) of 1,3,2-dioxaborinane **3** and 0.89 ml (11.5 mmol) methanesulphonyl chloride in 25 ml of anhydrous THF. After 1 h at 0°C the cooling bath was removed and the solution was stirred overnight at r.t. Subsequently, 3 ml of water was added and the mixture was then set to pH 7 by means of 10% HCl. The crude product was extracted from the mixture with chloroform (4×30 ml) and the combined organic layers were then dried (Na_2SO_4). Finally, evaporation of the solvents yielded 4.50 g (100%) of pure anhydride **4**. Mp. 201°C. IR (KBr): 2959, 2903, 1781, 1720, 1482, 1424, 1343, 1318, 1254, 1213, 1174, 1132, 1040, 1000, 709, 635 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.04 (s, 12H, CH_3), 3.80 (s, 8H, CH_2), 7.74 (d, 4H, *J* = 8.3 Hz, $H_{arom.}$), 8.12 (d, 4H, *J* = 8.3 Hz, $H_{arom.}$). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 21.9 (4 C, CH_3), 31.9 [2 $C_{quat.}$, *C*(CH_3)$_2$], 72.4 (4 C, CH_2), 129.4 (4 C, C-3,5), 130.4 ($C_{quat.}$, *C*-CO_2H), 134.1 (4 C, C-2,6), 139.4 (2 $C_{quat.}$, C-B), 162.6 (2 $C_{quat.}$, C=O). ^{11}B-NMR ($CDCl_3$, 128 MHz): δ = 26.6. MS(EI): *m/z* (%) 450 [M^+] (5), 422 (15), 217 (100), 194 (10), 104 (15). Calcd. for $C_{24}H_{28}B_2O_7$: C, 64.04; H, 6.27. Found: C, 64.23; H, 6.34.

1*H*-Benzotriazol-1-yl[4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenyl]methanone (5) Within 30 min, a solution of 3.69 g (31.0 mmol) of 1*H*-benzotriazole and 0.80 ml (11.0 mmol) thionyl chloride in 20 ml of anhydrous dichloromethane was added dropwise to a suspension of 2.34 g (10.0 mmol) acid derivative **3**. After an additional 60 min of stirring, the solid was filtered off and washed with dichloromethane (4×10 ml). The filtrate was neutralised with 10% aqueous NaOH. After extraction of the water layer with dichloromethane (3×10 ml), the combined organic phases were dried (Na_2SO_4) and evaporated to dryness. The product **5** thus obtained (2.70 g, 81%) turned out to be pure according to a proton NMR spectrum. Mp. 166°C. IR (KBr): 2959, 1703, 1487, 1476, 1422, 1370, 1368, 1339, 1307, 1305, 1245, 1140, 1130, 1054, 940, 887, 759, 642 cm^{-1}. ^{1}H-NMR (C_6D_6, 400 MHz): δ = 0.57 (s, 6H, CH_3), 3.37 (s, 4H, CH_2), 6.96 (ddd, 1H, *J* = 8.4, 7.5, 1.2 Hz, $H_{arom.,Bzt}$), 7.12 (ddd, 1H, *J* = 8.1, 7.5, 1.4 Hz, $H_{arom.,Bzt}$), 7.85 (ddd, 1H, *J* = 8.4, 1.4, 0.9 Hz, $H_{arom.,Bzt}$), 8.16 (d, 2H, *J* = 8.4 Hz, $H_{arom.}$), 8.20 (d, 2H, *J* = 8.4 Hz, $H_{arom.}$), 8.32 (ddd, 1H, *J* = 8.1, 1.2, 0.9 Hz, $H_{arom.,Bzt}$). ^{13}C-NMR (C_6D_6, 100 MHz): δ = 22.2 (2 C, CH_3), 32.1 [2 $C_{quat.}$, *C*(CH_3)$_2$], 72.8 (2 C, CH_2), 115.8 (C, Bzt), 120.8 (C, Bzt), 126.7 (C, Bzt), 130.7 (C, Bzt), 131.8 (2 C, C-3,5), 133.4 ($C_{quat.,Bzt}$, *C*NCO), 134.6 ($C_{quat.,phenyl}$, *C*-C=O), 134.8 (2 C, C-2,6), 139.7 ($C_{quat.}$, C-B), 146.9 ($C_{quat.,Bzt}$, CN=N), 167.7 ($C_{quat.}$, C=O). ^{11}B-NMR (C_6D_6, 128 MHz): δ = 26.5. MS(EI): *m/z* (%) 334 [*M*-H]$^+$ (10), 307 (70), 218 (100), 133 (20), 105 (35). Calcd. for $C_{18}H_{18}BN_3O_3$: C, 64.50; H, 5.41; N, 12.54. Found: C, 64.48; H, 5.42; N, 12.63.

4-(Trimethylsilyl)benzoic acid (6) Under an inert atmosphere, a solution of 1.6 M *n*-butyllithium in hexane was added dropwise to a solution of 8.02 g (35.0 mmol) (4-bromophenyl) trimethylsilane in 100 ml of anhydrous THF. Then the mixture was kept at the same temperature for 1 h. Subsequently, with careful control of the inert atmosphere, the whole mixture was poured onto a large excess of solid carbon dioxide (approximately 50 g) and was then allowed to warm up to r.t. within 2 h. After addition of 20 ml of water, pH 6 was adjusted applying 10% HCl. The aqueous phase was then extracted with dichloromethane (4×20 ml). Finally, the combined organic layers were dried (Na_2SO_4) and evaporated to dryness to yield 6.33 g (93%) of pure benzoic acid derivative **6**. Mp. 116°C. IR (KBr): 2957, 1689, 1553, 1419, 1388, 1315, 1293, 1252, 1187, 1095, 945, 840, 808, 742, 699 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 0.31 [s, 9H, $Si(CH_3)_3$], 7.65 (d, 2H, *J* = 8.0 Hz, $H_{arom.}$), 8.09 (d, 2H, *J* = 8.0 Hz, $H_{arom.}$); carboxylic proton not detected due to exchange reaction. ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = -1.4 [3 C, $Si(CH_3)_3$], 129.1 (2 C, C-2,6), 129.4 ($C_{quat.}$, *C*-CO_2H), 133.4 (2 C, C-3,5), 148.1 ($C_{quat.}$, $C_{arom.}$Si), 172.6 ($C_{quat.}$, COOH). MS(EI): *m/z* (%) 194 [M^+] (10), 179 (100), 133 (15), 119 (10), 91 (20), 77 (18), 73 (25).

1*H*-Benzotriazol-1-yl[4-(trimethylsilyl)phenyl]methanone (7) The trimethylsilyl compound **7** was obtained in analogy to the preparation of the organoboron derivative **5** in 98.5% yield, starting from 2.85 g (23.9 mmol) benzotriazole, 0.62 ml (8.49 mmol) thionyl chloride, and 1.50 g (7.72 mmol) acid derivative **6**. Mp. 101°C. IR (KBr): 1706, 1389, 1378, 1367, 1289, 1228, 1041, 937, 836, 834, 757, 741, 729 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 0.34 [s, 9H, $Si(CH_3)_3$], 7.56 (ddd, 1H, *J* = 8.3, 7.2, 1.0 Hz, $H_{arom.,Bzt}$), 7.72 (ddd, 1H, *J* = 8.2, 7.2, 1.0 Hz, $H_{arom.,Bzt}$), 7.74 (d, 2H, *J* = 8.2 Hz, $H_{arom.}$), 8.16 (d, 2H, *J* = 8.2 Hz, $H_{arom.}$), 8.18 (d, 1H, *J* = 8.3 Hz, $H_{arom.,Bzt}$), 8.40 (d, 1H, *J* = 8.2 Hz, $H_{arom.,Bzt}$). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = -1.4 [3 C, $Si(CH_3)_3$], 114.8 (C, Bzt), 120.2 (C, Bzt), 126.3 (C, Bzt), 130.4 (C, Bzt), 130.5 (2 C,

C-2,6), 131.5 ($C_{quat.,phenyl}$, *C*-C=O), 132.3 ($C_{quat.,Bzt}$, *C*NCO), 133.3 (2 C, C-3,5), 145.8 ($C_{quat.,Bzt}$, CN=N), 148.1 ($C_{quat.}$, $C_{quat.}$Si), 167.0 ($C_{quat.}$, C=O). MS(EI): *m/z* (%) 295 $[M]^+$ (17), 267 (21), 252 (98), 177 (100), 73 (85). Calcd. for $C_{16}H_{17}N_3OSi$: C, 65.05; H, 5.80; N, 14.22. Found: C, 65.08; H, 5.88; N, 14.13.

Chemical wood modification procedure

In general, 7 mmol of the appropriate wood modifying reagent was applied per 1 g of wood. Thus, all reactions were performed in 10 ml of anhydrous dimethylformamide (DMF) with 0.3 ml triethylamine and 10 mol% of 4-dimethylaminopyridine under nitrogen atmosphere: (1) with wood meal (0.150 g, approximately 500 μm in diameter) of beech heartwood, pine sapwood, or spruce heartwood, or (2) with veneer chips of pine sapwood (approximately 45 mm×25 mm×0.8 mm; approximately 1.15 g, adapted equivalents of all reagents). As a standard pre-treatment, prior to modification, wood was extracted for 24 h in a Soxhlet apparatus with a solvent mixture comprising toluene/acetone/methanol 4:1:1, to assure well-defined laboratory conditions. Additionally, the extracted wood was oven-dried at 105°C overnight and then stored in a laboratory desiccator. Initially, the wood modification reactions were conducted for 16 h at 150°C to ensure complete reaction, but with regard to industrial applicability also 120°C has been successfully applied. After this reaction time, the mixture was allowed to cool down to r.t. and the modified wood subsequently was filtered off by means of a Buchner funnel (equipped with a dried and weighed filter paper). The wood was then washed subsequently with each 100 ml water, THF, and diethyl ether. Finally, the now modified wood material was dried at 105°C for 16 h and then cooled down to r.t. in a desiccator.

Results and discussion

Chemical syntheses of wood modification reagents

For comparison with classical acylation by means of acetic anhydride, the corresponding anhydride of a boron-bearing coupling component was prepared. The commercially available 4-methylphenylboronic acid (**1**) was the initial compound, which was also obtained synthetically in our laboratory in a multigram scale (0.25 mol and above) from 4-lithiotoluene and an appropriate trialkyl borate in 63% yield. The subsequent oxidation of the methyl group within **1** was performed by $KMnO_4$ in aqueous NaOH under phase-transfer catalysis conditions, similar to a protocol for the *ortho*-substituted analogue (Tao 2002). Thus, 4-carboxyphenylboronic acid (**2**) was obtained in 85% yield. Due to the air stability of cyclic boronic esters (Ishihara and Yamamoto 2005), the free organoboronic acid was then quantitatively esterified with 2,2-dimethyl-1,3-propanediol at ambient temperature to furnish the boronate **3**, a compound that previously had been prepared in only 26% yield (McCormick and McElhinney 1976). Finally, the anhydride **4** was formed in quantitative yield upon treatment of 2-(4-carboxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (**3**) with methanesulphonyl chloride and triethylamine in anhydrous THF (Figure 1a).

Subsequently, an alternative activation of the organometal compounds was developed via the less cost-intense reagent benzotriazole (e.g., Katritzky 2002) instead of the routine anhydride method. A 1*H*-benzotriazole-modified carboxylic acid was an active coupling unit, attached to the aromatic 4-position of a biocidal phenylboronic ester (Figure 2).

It is worthy to note that the release of free benzotriazole in the course of the reaction is not problematic as this compound is water soluble and can be easily removed by a washing step subsequent to modification. Furthermore, it is assumed that slight residues within wood would cause additional preservation properties based on the known pharmaceutical applicability of benzotriazole and its derivatives as antifungal and antibacterial agent (Al-Omran et al. 2002).

In a further step, the synthesis was started with aromatic acid **3** via 4-methylphenylboronic acid (**1**) and its protection was realised by means of the diol, but finally, the carboxy group of **3** was activated by benzotriazole to yield the hitherto unknown compound **5** in 81% yield (Figure 1b), which serves as wood modification reagent. Then, this benzotriazole method was extended to the silyl derivative **7**. Arylsilanes are well-known precursors for electrophilic *ipso*-substitutions, such as borylation reactions. The replacement of boron by silicon appears to be very interesting not only for chemical reasons but also in view of the antifungal and hydrophobic properties of organosilyl substances in wood (Donath et al. 2004; Mai and Militz 2004). Compound **7** was obtained from (4-bromophenyl)trimethylsilane via lithiation and carboxylation to 4-(trimethylsilyl)benzoic acid (**6**), and final activation with benzotriazole (Figure 1c).

Weight percent gain (WPG) after modification

Wood modification was accomplished on extracted milled wood as well as extracted veneer chips, to avoid side reactions with extractives. The WPG values are summarised in Table 1.

Subsequent to chemical modification, the wood samples were subjected to a further Soxhlet extraction to confirm the presumed strong chemical bonding of the organic biocide; no weight loss was observed.

IR spectroscopic characterisation

Figure 3 depicts the FT-IR spectra (in KBr pellets) of unmodified beech wood (I) in comparison to boronated material, which was prepared by means of the classical anhydride procedure (II) or the novel benzotriazole method (III), as well as silyl-modified wood (IV). Aside from the typically broad C-O stretch region from 1000 to almost 1200 cm^{-1}, some remarkable characteristic IR bands occur.

Boronated wood On the one hand, the particular carbonyl band above 1700 cm^{-1} shows small but nonetheless significant changes that perspicuously indicate wood modification (region "A" in Figure 3). On the other hand, a characteristic shift of the corresponding C-O vibration from 1244 cm^{-1} (untreated beech wood) to 1268 cm^{-1} is found in region "B" within both of the IR spectra of the boron-modified wood. An additional and unambiguous indicator for the successful boronation is the presence of the boron-carbon vibration band "C" at 711 cm^{-1}.

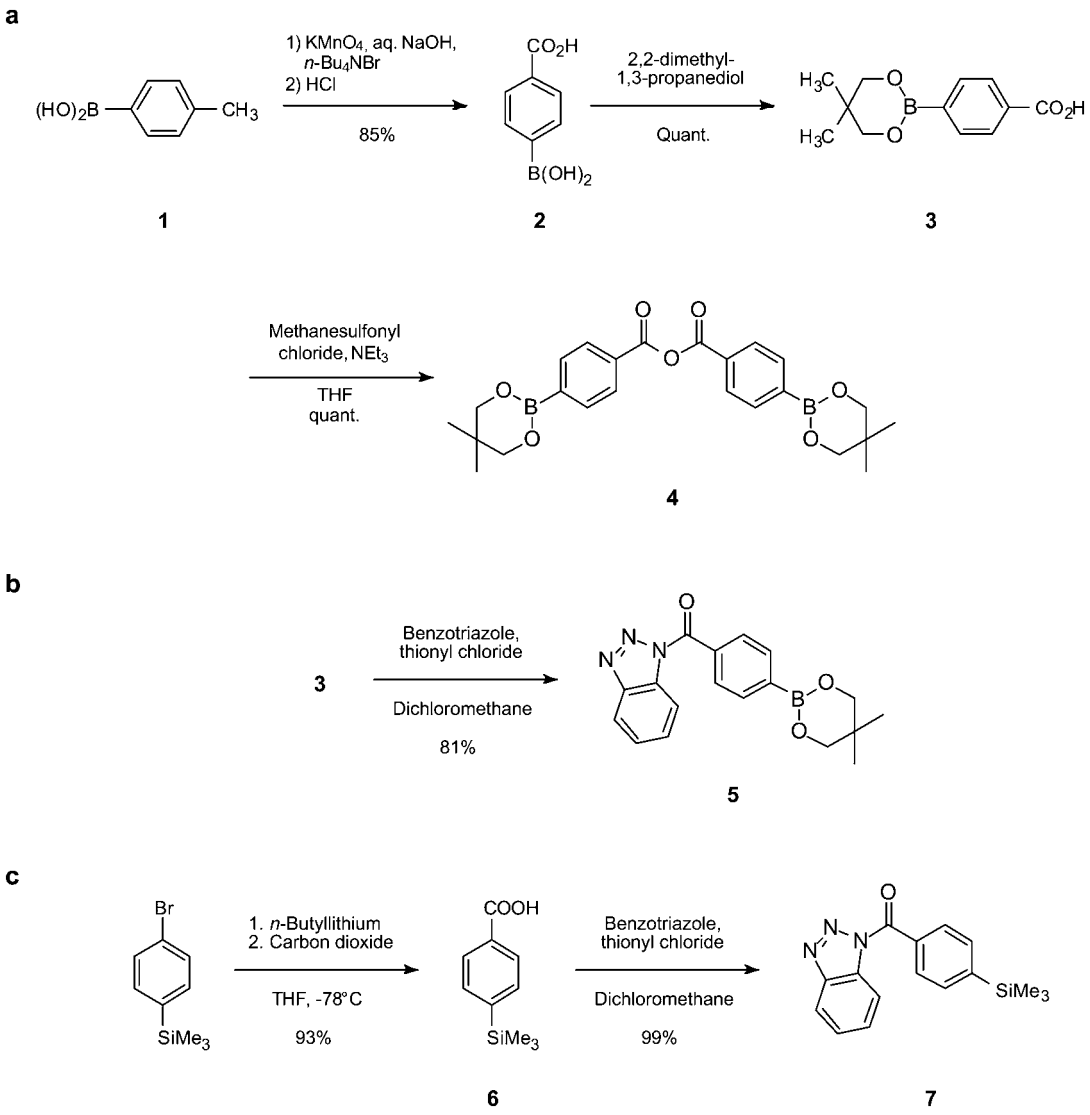

Figure 1 Synthesis of boron- or silicon-containing wood preservatives.

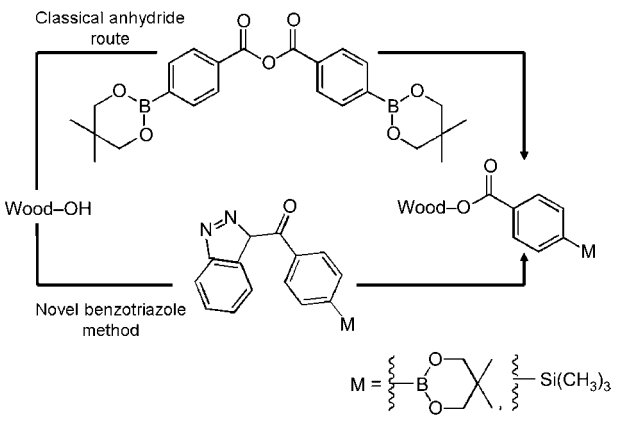

Figure 2 Reaction of wood with a 1*H*-benzotriazolyl-activated derivative of the biocide.

Table 1 Weight percent gain (WPG) values of chemical wood modification.

	Boron-modification		Silicon-modification
Wood	Classical anhydride method	Novel benzotriazole method	Novel benzotriazole method
Beech meal (150°C)	15.0	21.5	24.8
Spruce meal (150°C)	17.7	25.2	31.0
Pine meal (150°C)	13.8	19.8	24.0
Pine meal (120°C)		19.5	24.1
Pine veneer (120°C)		16.6	19.5

Silyl-modified wood In addition to a single asymmetric C-H stretching band of the trimethylsilyl group at 2952 cm^{-1} (beyond the depicted zoom in Figure 3), the carbonyl vibration in spectrum IV is shifted to 1731 cm^{-1} compared to 1742 cm^{-1} in the case of untreated wood. Additionally, the C-O stretching region ("B") is overlapped by a single peak at 1251 cm^{-1} due to the C-H deformation vibration of the Si-CH_3 group. Furthermore,

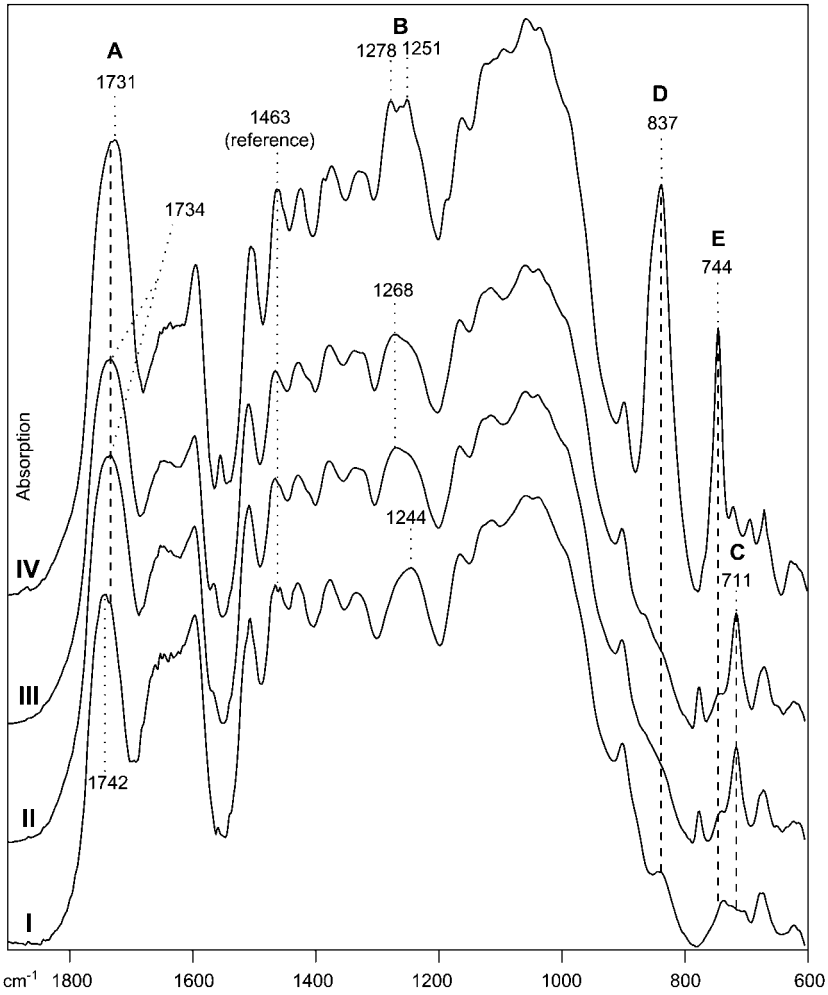

Figure 3 IR spectra of beech wood: untreated (I), boron-containing (II, III), and silyl-modified (IV).

the silyl-modified wood shows two bands at 837 cm^{-1} ("D", C-H rocking motion within the Si-CH_3 group) and 744 cm^{-1} ("E", Si-C vibration).

Semi-quantitative IR analysis The gravimetrically determined WPG increase (Table 1) was compared to the increase of the carbonyl IR band at approximately 1737 cm^{-1}, which occurs from the introduced ester group during wood modification with the boron-bearing precursor (classical anhydride approach, then novel method) and the silyl derivative, respectively. The IR spectra are discussed semi-quantitatively, because more accurate results a priori are limited by different possible sources of error, e.g., reflection and interference effects, inadequate temperature control, or lacking detector linearity. To obtain the most comparable results, the post-processing of the IR spectra was kept to a minimum. Thus, the absorption mode spectra were baseline-corrected applying the standard rubber band method and were normalised to the highest band at approximately 1050 cm^{-1}. Due to the use of a stacked plot which involves a shifted alignment of the spectra parallel to the ordinate, no absorbance scale is given in Figure 3. The apparent increase of the carbonyl band within spectra I to IV reflects the growth of the corresponding WPG values given in Table 1. More detailed information was obtained dividing the individual carbonyl band height by the corresponding height of the C-H deformation vibration of the wood backbone at approximately 1463 cm^{-1} (internal reference). Ranging from spectrum I to spectrum IV, this procedure results in band height ratios (Stefke et al. 2008) of 0.96, 1.06, 1.07, and 1.12, respectively, which also reflect the WPG tendency shown in Table 1.

Conclusions

Boric acid and borates applied to date for wood protection are leachable, as these boron substances are almost not chemically bound but just spread. Additionally, even rarely formed BO-C bonds are hydrolysed easily. The B-C(sp^3) bond of alkylboronic acids are known to be quite unstable towards oxidation. Hence, a simple alteration of one of the standard chemical modification methods, such as esterification by means of boryl-substituted acetic acid, is unsuitable.

In the present work, a novel concept was developed comprising covalent attachment of a boron-containing organic compound to wood. An appropriate aromatic boronic acid ester was selected, which serves as the boron-bearing active site. The B-C(sp^2) bonds of arylboronic acids are quite stable both to hydrolysis and oxidation. Fixation of this biocidal moiety to wood was accomplished by esterification via an additional benzo-

triazolyl-activated carboxylic acid group. This method was finally expanded to a silyl-bearing counterpart. Arylsilanes are interesting precursors for subsequent *ipso*-substitution reactions. The WPGs after modification are satisfactory to excellent. Of course, the route from laboratory experiments with wood meals and veneer chips to industrial application is still lengthy. Details concerning the penetration depth, the effectiveness against microorganisms, the economic viability of the process, just to mention a few, have to be clarified. Corresponding investigations are underway in our laboratory.

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